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(19)

(54) IMPROVEMENTS IN OR RELATING TO MINERAL FILLERS

(71) We, ENGLISH CLAYS LOVERING POCHIN & COMPANY LIMITED, a British Company, of John Keay House, St. Austell, Cornwall, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to mineral fillers and, more particularly, is concerned with a white clay filler suitable for use in the manufacture of a paper or the like product.

In the manufacture of a paper or the like product, there is generally incorporated in the fibrous pulp from which the paper or the like product is formed a mineral filler the use of which *inter alia* reduces the cost of the product . One mineral filler which is used for this purpose is kaolin which is a white clay which also brings about an improvement in the opacity and printing properties of the paper or the like product. However, the kaolin fillers conventionally used result in a reduction in the strength of a paper or the like product containing them.

According to one aspect of the present invention there is provided a filler, for a paper or the like product comprising particles of a white clay having (a) a particle size distribution such that it contains not more than 18% by weight of particles smaller than 2 microns equivalent spherical diameter, (b) an abrasion of less than 120 Valley, and (c) a brightness (measured as the percentage reflectance to light of wavelength 457 nm) of at least 76.

According to another aspect of the present invention there is provided a method of preparing a filler for a paper or the like product which comprises: subjecting a white clay mineral to a particle size classification process in order to obtain a product containing not more than 18% by weight of particles smaller than 2 microns equivalent spherical diameter; if necessary subjecting said white clay mineral to a beneficiation process in order to reduce the number of particles having an abrasive character to a level such that the product has an abrasion of less than 120 Valley; and removing or bleaching sufficient iron-containing impurities present in said white clay mineral to ensure that the white clay filler has a brightness of at least 76 (measured as the percentage reflectance to light of wavelength 457 nm).

According to a further aspect of the present invention there is provided a paper or the like product containing a white clay filler, wherein said paper or the like product contains a quantity of said white clay filler such that said paper or the like product has a burst strength which is at least 60% of the burst strength of the unfilled paper or the like product and wherein the white clay filler comprises particles of a white clay having (a) a particle size distribution such that the white clay filler contains less than 18% by weight of particles smaller than 2 microns equivalent spherical diameter, (b) an abrasion of less than 120 Valley, and (c) a brightness (measured as the percentage reflectance to light of wavelength 457 nm) of at least 76.

In carrying out the method of the invention the particle size classification process is preferably carried out as a two stage gravitational or centrifugal sedimentation process. Furthermore, benefication of the clay filler is advantageously carried out by subjecting it either to a froth flotation process, generally using a cationic collector whereby the kaolin particles are caused to float and the quartz and other abrasive mineral impurities to sink to the bottom of the flotation cell, or to a two phase separation process of the type described in British Patent Specifications Nos. 1,222,508 and 1,475,881. In order to obtain a white clay having the required brightness, the iron-containing impurities are preferably removed by a

magnetic separation process and/or bleached by a reducing bleaching process.

In one embodiment of the method of the invention the following steps are carried out:

(i) a slurry of a raw kaolin is treated to remove grit;

(ii) the degritted kaolin slurry is deflocculated and subjected to a particle size classification process by gravitational or centrifugal sedimentation to produce a fine, paper coating-grade kaolin and a coarse kaolin;

(iii) the coarse kaolin is subjected to at least one further particle size classification process to reduce the percentage by weight of particles having an equivalent spherical diameter smaller than 2 μm in the coarse kaolin to below 18%

(iv) the coarse kaolin product of step (iii) is subjected to a beneficiation process to reduce the proportion of abrasive particles;

(v) the beneficiated coarse kaolin is subjected, in the form of an aqueous slurry, to a process such that discolouring iron-containing impurities are removed or rendered lighter in colour; and

(vi) the product of step (v) is dewatered in such a way as to minimise the formation of particles having an equivalent spherical diameter smaller than 1 μm and to produce a white clay filler containing less than 25% by weight water.

Prior to step (i), the slurry of raw kaolin is usually thickened to a specific gravity in the range 1.050 to 1.100.

In step (i) the removal of grit is conveniently achieved by removing substantially all particles coarser than 50 microns.

In step (ii) the degritted kaolin slurry may be deflocculated with thread of a dispersing agent, for example a water-soluble condensed phosphate salt, a water-soluble salt of a polysilicic acid, or an organic polymeric dispersing agent such as a water-soluble salt of a polyacrylic acid having a number average molecular weight not greater than 10,000 or a water-soluble copolymer deflocculant of the type disclosed in British Patent Specification No. 1,414,964.

In step (iii), the particle size classification process is conveniently performed by gravitational or centrifugal sedimentation and generally under conditions such that, in theory, all particles having an equivalent spherical diameter larger than d μm, where d is selected to be in the range from 4 to 12, should report to the coarse fraction. It is necessary to carry out at least one further particle size classification process because, when using a sedimentation process in practice, many particles having an equivalent spherical diameter considerably smaller than d μm are carried into the coarse fraction with the larger particles. Only one further particle size classification process is generally required as this is usually sufficient to reduce the percentage by weight of particles having an equivalent spherical diameter smaller than 2 μm to below 18%. Preferably, the particle size classification process is carried out in a manner reducing the percentage by weight of particles having an equivalent spherical diameter smaller than 1 μm to 10% or less.

The mineral beneficiation process of step (iv) is conveniently a froth flotation process or a two liquid phase separation process. In either case a cationic collector reagent is used to render the kaolinite particles hydrophobic so that in the case of froth flotation process they report to the froth, and in the case of the two liquid phase separation process they report to the interface between the aqueous medium and the non-polar organic liquid, while the abrasive impurity particles remain in the aqueous medium. The abrasion of the beneficiated kaolin as measured by the Valley abrasion test should be less than 120, and preferably less than 100. The Valley abrasion test as used herein is carried out in the following manner: The apparatus used comprises a machine which rubs a slurry of the test material over the surface of a rectangular piece of paper machine "wire" (i.e. wire mesh), thus causing the wire to wear. Essential components of the apparatus are a flat perforated support plate for the piece of wire and a frame to clamp the wire firmly in place, a circulating system to supply the slurry of the test mterial at a constant rate to the upper surface of the wire, a weighted brass block with a perforated base made of a synthetic plastics material to distribute the slurry over the surface of the wire, and a suitable motor arrangement to operate the circulating pump and to move the weighted block back and forth across the surface of the wire. It is the sliding action of the weighted block on the wire, with the slurry of the test material at the interface, which causes the wire to wear. The paper machine wire used in the test is 60 mesh × 60 mesh plain weave phosphor bronze wirecloth with a wire diameter of 0.17 mm and each piece is cut to the dimensions 9½ inches × 4¾ inches (241mm × 121mm). The weighted block has a total weight, not including the driving arm, of 19.5 lb (8.85kg) and the perforated base is formed from a linen-reinforced phenol-formaldehyde resin material which is marketed under the Trade mark "TUFNOL", the area in contact with the wire having the dimensions 3 1/16 inches × 3¾ inches (78mm × 95mm). The weighted block is reciprocated by means of a driving arm sliding in an elongated bearing to ensure accurate rectilinear motion. The driving arm is actuated

through a connecting rod by a driving wheel which is rotated in a horizontal plane by the motor arrangement. The speed of reciprocation of the weighted block is 95 cycles per minute and the stroke is 4 inches (102mm) so that the total wearing area on the piece of wire is 3 1/16 inches × 7¾ inches (78 mm × 197 mm).

The slurry of the test material is prepared by dispersing 75g of the test material in cold water, screening the suspension through a No 150 mesh B.S. Sieve (nominal aperture 104 μm), making the volume of the screened suspension up to 2400 ml with cold water and correcting the pH to 5.0 with dilute acid or alkali as necessary.

To carry out the Valley abrasion test, a rectangular piece of wire of the dimensions and type described above is washed in cold water and any loose pieces are removed. The wire is then dried in an oven at 80°C for 30 minutes and allowed to cool in a desiccator for 10 minutes. The weight of the piece of wire is then determined to the nearest milligram. The piece of wire is laid on the perforated support plate and clamped firmly in place with the frame. The slurry is circulated through the perforated base of the weighted block, the piece of wire and the perforated supported plate at a steady flow rate of 850 ml/min and the weighted block is set into motion and allowed to continue until 6000 cycles have been completed. The motor is then switched off and the wire removed, washed and dried as before, and the weight determined to the nearest milligram. The loss in weight in milligrams of the piece of wire gives a measure of the abrasiveness of the test material, but in order to allow for possible variations in the properties of the pieces or wire, the loss in weight of a second piece of wire which is as nearly as possible identical to the first piece is determined under the same conditions but using a slurry containing a standard material of known Valley abrasion. The Valley abrasion of the test material is then calculated by means of the formula.

$$A_t = A_s \cdot \frac{W_t}{W_s}$$

Where At_t is the Valley abrasion of the test material
A_s is the Valley abrasion of the standard material
W_t is the loss of weight of the wire using the test material
W_s is the loss of weight of the wire using the standard material.

In step (v) of the method of the invention, the undesired effect of discolouring iron-containing impurities is preferably ameliorated by means of either magnetic separation or chemical solution. In the case of magnetic separation, in order to achieve a good combination of high extraction of discoloring impurities and a good throughput rate, the magnetic field intensity is preferably at least 10,000 gauss. In the case of chemical solution of the iron-containing impurities this is preferably effected by treating an aqueous suspension of the beneficiated kaolin obtained at the end of step (iv) with a reducing agent such as sodium or zinc dithionite, which reduces the iron to the ferrous state and renders it soluble in water. If necessary a combination of magnetic separation and chemical solution may be used. The reflectance to light of 457 nm wavelength of the product of step (v) should be at least 76.0 and preferably at least 78.0 as measured, by an ELREPHO brightness meter, in accordance with ISO standard Nos. 2469, 2470 and 2471. The word "ELREPHO" is a Trade Mark.

In step (vi) the aqueous slurry obtained at the end of step (v) is preferably dewatered by pressure filtration at a pressure in excess of 150 psig to give a dewatered product containing less than 25%, and preferably less than 20%, by weight of water. A tube pressure filter such as is described in British Patent Specification No. 1,240,465 is very suitable for carrying out this step. A thermal drying step may be used after the pressure filtration step provided that very little mechanical work is performed on the filter cake and the surface temperature of the material is not allowed to exceed 120°C. A suitable drier would be a hand drier in which a filter cake is deposited without further mechanical treatment, such as extrusion or pelletising, on a moving wire mesh belt and passed through a heated zone in which the temperature is such that the surface temperature of the material does not exceed 120°C.

The product of the method of the invention when incorporated in a stock of paper fibres should give a paper which has a burst strength which is at least 60% of the burst strength of unfilled paper formed from the same fibres at a loading of about 17% by weight or less of the filler.

The invention is illustrated by the following Example

Example

A white clay filler for paper was prepared in the following manner:

An aqueous slurry of raw kaolin, containing mica, quartz and feldspar as impurities, was

thickened to a specific gravity in the range 1.050 and 1.100 and then degritted to remove substantially all particles having a diameter greater than 53 μm. The thickened slurry of degritted kaolin was deflocculated with a sodium polyacrylate dispersing agent having a number average molecular weight of 1,650 and the resulting deflocculated slurry subjected to a particle size classification process in a scroll-type centrifuge under conditions such that, in theory, all particles having an equivalent spherical diameter larger than 5 μm should report to the coarse fraction. The classification process in fact produced a fine paper coating grade kaolin and a coarse kaolin having the properties of a conventional paper filler and still containing about 20% by weight of particles having an equivalent spherical diameter smaller than 1 μm.

The coarse product was subjected to a further similar particle size classification step in a second scroll type centrifuge and the coarse kaolin obtained as a result of this second classification process was subjected to a froth flotation process using octadecylamine acetate as the cationic collector reagent so that the substantially non-abrasive kaolinite and mica particles were caused to float and the abrasive particles, predominantly quartz and feldspar sank to the bottom of the flotation cells. The froth product comprising approximately 50% by weight of the feed to the froth flotation step was sprayed with water to break the froth and the resultant aqueous suspension was subjected to magnetic separation in a high intensity magnetic separator which comprised a separating chamber packed with steel wool and electromagnet coils for establishing in the region of the separating chamber a magnetic field of about 20,000 gauss.

The impurities extracted in the magnetic separation step were predominantly iron-containing mica particles. The non-magnetic product was found to have an acceptable reflctance to violet light but also had a yellowness, as measured by the difference between the reflectance to yellow light of wavelength 374 nm and the reflectance to violet light of wavelength 457 nm. This was probably due to very finely divided iron impurities. The non-magnetic product was blended with about 25% of its own weight of the coarse product of the second particle size classification process and the blended suspension was then treated with 3 Kg. of sodium dithionite per tonne of dry material in order to bleach the kaolin.

The blended and bleached aqueous slurry was then dewatered in a tube pressure filter at a pressure of 1200 psig to produce a filter cake of the desired filler containing 16% by weight of water.

The foregoing process is represented diagrammatically in the accompanying drawing.

The reflectance to visible light of wavelength 457 nm and 574 nm and the particle size distribution of the material at various stages of the process are set forth in Table 1 below.

TABLE 1

Material	Reflectance to light of wavelength		% by wt. of particles having an E.S.D. smaller than	
	457 nm	574 nm.	2 μm	1 μm
Coarse product of second classification step	72.5	79.9	6	3
Froth flotation product	73.8	82.0	7	4
Non-magnetic product	78.4	87.3	10	6
Blended product	75.5	84.1	9	5
Chemically bleached product	78.5	85.2	9	5
Tube pressure filter cake	78.5	85.2	13	7

The tube pressure filter cake was found to have an abrasion value as measured by the Valley abrasion test described above of 73.

An aqueous suspension containing 2% by weight of fibres obtained by treating and refining a bleached sulphite pulp was mixed in a stirred tank with 1.5% by weight, based on the weight of dry fibes, of a fortified rosin size and 3% by weight, based on the weight of dry fibres, of powdered aluminium sulphate. The resultant suspension of sized fibres was

diluted with water to 1% by weight of fibres and a flocculated suspension of a white clay filler according to the invention and prepared by the method described above was added in various proportions to give different loadings of the filler on the fibres.

The various mixtures were fed to the head box of a Fourdrinier paper machine on which, for each loading of clay, a web of paper was formed on the wire, dewatered and thermally dried. Samples of the web for each loading of clay were weighed dry and then incinerated and the weight of ash was used to calculate the percentage by weight of filler in the dry paper, after allowing for the loss of ignition of the clay.

Other samples of each paper were tested for their burst strength by the test prescribed in T.A.P.P.I. Standard T401 os-74. The burst strength is defined as the hydrostatic pressure in kilonewtons per square metre required to produce rupture of the material when the pressure is increased at a controlled constant rate through a rubber diaphragm to a circular area 30.5 mm in diameter. The area of the material under test is initialy flat and is held rigidly at the circumference but is free to bulge during the test.

The burst strengths were divided by the weight per unit area of the paper to give a bust ratio and the burst ratio for each sheet of filled paper was then expressed as a percentage of the burst ratio for a sheet of paper prepared from the same fibre stock but containing no filler.

The experiments described above were then repeated but using a conventional kaolin filler which had a particle size distribution such tht 51% by weight consisted of particles having an equivalent spherical diameter small than 2 μm and 38% by weight consisted of particles having an equivalent spherical diameter small than 1 μm. The reflectance to light of 457 nm wavelength was 81.0 to light of 574 nm wavelength 86.7. The results are set forth in Table II below.

TABLE II

% by wt. of filler (Based on dry filler wt.)	Burst ratio (% of unfilled paper burst ratio	
	filler in accordance with invention	conventional filler
5	87	84
10	75	70
15	65	59
20	57	49
25	49	39

It will be seen that the filler in accordance with the invention gives a higher strength for a given loading in the paper than the conventional filler. Alternatively a greater amount of the filler in accordance with the invention can be incorporated in the paper for a given reduction in strength.

The reflectance to light of 457 nm was measured for the samples of paper and it was discovered that, for a given loading of filler, the reflectance of the paper containing the filler in accordance with the invention was the same as that of the paper containing the conventional filler within the limits of experimental accuracy.

WHAT WE CLAIM IS:-

1. A filler, for a paper or the like product, which comprises particles of a white clay having (a) a particle size distribution such that it contains not more than 18% by weight of particles smaller than 2 microns equivalent spherical diameter, (b) an abrasion of less than 120 Valley, and (c) a brightness (measured as the percentage reflectance to light of wavelength 457 nm) of at least 76.

2. A filler as claimed in claim 1, wherein said white clay has a particle size distribution such that it contains not more than 10% by weight of particles smaller than 1 micron equivalent spherical diameter.

3. A filler as claimed in claim 1 or 2, wherein said white clay has an abrasion of less than 100 Valley.

4. A paper or the like product wherein said paper or the like product contains a quantity of a white clay filler such that said paper or the like product has a burst strength which is at least 60% of the burst strength of the unfilled paper or the like product and in that the white clay filler comprises particles of a white clay having (a) a particle size

distribution such that the white clay filler contains less than 18% by weight of particles smaller than 2 microns equivalent spherical diameter, (b) an abrasion of less than 120 Valley, and (c) a brightness of at least 76 (measured as the percentage reflectance to light of wavelength 457 nm).

5. A method of preparing a filler for paper or the like which comprises the steps of subjecting a white clay mineral to a particle size classification process in order to obtain a product containing not more than 18% by weight of particles smaller than 2 microns equivalent spherical diameter; if necessary subjecting said white clay mineral to a beneficiation process in order to reduce the number of particles having an abrasive character to a level such that the product has an abrasion of less than 120 Valley; and removing or bleaching sufficient iron-containing impurities to ensure that the white clay mineral has a brightness of at least 76 (measured as the percentage reflectance to light of wavelength 457 nm).

6. A method according to claim 5, wherein the particle size classification process is carried out as a two-stage gravitational or centrifugal sedimenation process.

7. A method according to claim 5 or 6 wherein said method comprises the steps of

(i) treating a slurry of raw kaolin clay to remove grit therefrom;

(ii) deflocculating the degritted kaolin slurry and subjecting it to a particle size classification process by gravitational or centrifugal sedimentation to produce a fine, paper coating-grade kaolin and a coarse kaolin;

(iii) subjecting the coarse kaolin to at least one further particle size classification process to reduce the percentage by weight of particles having an equivalent spherical diameter smaller than 2 μm in the coarse kaolin to below 18%;

(iv) beneficiating the coarse kaolin product of step (iii) to reduce the proportion of abrasive particles to a level such that the coarse kaolin has an abrasion of less than 120 Valley;

(v) subjecting the beneficiated coarse kaolin in the form of an aqueous slurry to a process such that discolouring iron-containing impurities are removed or rendered lighter in colour; and

(vi) dewatering the product of step (v) in such a way as to minimise the formation of particles having an equivalent spherical diameter smaller than 1 μm and to produce a white clay filler containing less than 25% by weight water.

8. A method according to claim 7, wherein prior to step (i) the slurry of raw kaolin is thickened to a specific gravity in the range of from 1.050 to 1.100.

9. A method according to claim 7 or 8, wherein in step (i) substantially all particles coarser than 50 microns are removed.

10. A filler as claimed in claim 1, substantially as described in the foregoing Example.

11. A paper or the like product as claimed in claim 4 substantially as described in the foregoing Example.

12. A method, according to claim 5, of preparing a filler, substantially as described in the foregoing Example.

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C[illegible]LETE SPECIFICATION

This drawing is a reproduction of the Original on a reduced scale